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ELECTROPHOTOGRAPHIC TONER
[Denshi shashin-yo tonaa]

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Specification

1. Title of the Invention

Electrophotographic toner

2. Claims

1. Electrophotographic toner characterized by the fact that a conductive polymer is adhered to the surface of a core substance comprising toner.

2. Electrophotographic toner described in Claim 1 characterized by the fact that the conductive polymer is comprised of aniline, pyrrole, thiophen, or their derivatives.

3. Detailed Explanation of the Invention

(Industrial Field of Application)

This invention pertains to toner for developing electrostatic latent images in electrophotography. More particularly, this invention pertains to a novel electrophotographic toner in which a conductive polymer that can function as a substance imparting conductivity is adhered to the surface of a core substance.

(Prior Art)

Electrophotography generally employs the method of forming a latent image on a photoelectric unit comprised of components that include a photoelectric substance, developing this by a powdered developing agent to render it visible, then fixing onto paper by heat or pressure, or in some cases, by a solution. Developing agents for such electrophotography can be broadly divided into ① one-component developing agents in which

components such as a magnetic substance, coloring agent, substance imparting conductivity, charge regulator, and fluidity improving agent are dispersed in a binder resin, and ② two-component developing agents comprised of a mixture of a toner containing a coloring agent, substance imparting conductivity, charge regulator, and fluidity improving agent dispersed in a binder resin, and an iron powder or ferrite powder carrier.

Two-component developing agents achieve developing by toner charged by friction with the carrier adhering to an electrostatic latent image. Magnetic toners used in one-component developing agents also differ in their resistance. Conductive toner adheres by inducing a reverse polarity charge by electrostatically charging the photosensitive unit, while high-resistance toner adheres to the photosensitive unit by polarizing or injecting a charge within the same toner grains. Furthermore, insulating toner that charges similarly to two-component developing agents is also used. This adheres to the photosensitive unit by a part used to feed toner or by charging toner by friction between toner grains. Conductive grains are used as a substance imparting conductivity to control the conductivity and/or insulating resistance affecting the amount of frictional electrostatic charge of this type of toner.

(Problems that the Invention is to Solve)

Carbon black is used as the abovementioned substance imparting conductivity and also plays the role of a coloring agent. However, because carbon black absorbs a large amount of moisture, adding too much carbon black, especially to two-component developing agents, reduces transfer in high-humidity atmospheres, while adding too little causes

problems such as the amount of electrostatic charge becomes unstable and has a negative effect on the image. One-component developing agents, moreover, are restricted in adding more conductive grains such as carbon black or graphite to toner already containing a large amount of magnetic substance and coloring agents. Furthermore, because conductivity is a surface phenomenon, frequently, a layer such as carbon black is formed on the surface of the core substance comprising the toner to create a conductive layer. To adhere these conductive grains to this surface and stabilize conductivity, however, requires taking complicated steps such as carbon black or other grains must be fused onto this surface.

The purpose of this invention is to enhance toner value by correcting problems in prior art such as these.

(Means of Solving the Problems)

As a result of various studies to achieve the purpose given above, the present inventors made the novel finding that toner that contains a conductive polymer adhered to the surface of a core substance has superior properties that can adequately meet the purpose given above, and so perfected the present invention.

That is, this invention is an electrophotographic toner characterized by the fact that a conductive polymer that is an oxidation polymer of aniline, pyrrole, thiophen, or their derivatives is adhered to the surface of a core substance comprising toner.

The conductive polymer of this invention is obtained by oxidation polymerization of aniline, pyrrole, thiophen, or their derivatives. Said "derivatives" are defined as compounds in which site 2 or 3 of aniline or site 3 or 4 of pyrrole and thiophen is substituted by an alkyl group or alkoxy group that has 1 to 18 carbon atoms.

As the method for adhering a conductive polymer to the surface of a core substance, by immersing a core substance in a solvent comprised of one type or two or more types of water, methanol, ethanol, propanol, or acetonitrile, then agitating in the presence of one type or two or more types of aniline, pyrrole, thiophen, or their derivatives (hereinafter abbreviated as "monomers") at a temperature of -40 to 50°C for 1 to 10 minutes, an oxidation polymer of said monomers is adhered to the surface of the core substance, and an electrophotographic toner is manufactured.

Solvents other than water, methanol, ethanol, propanol, and acetonitrile can be used in the method described above, but this increases the percentage of monomer oxidation polymer that drops out of the treatment solution and becomes unavailable to adhere to the core substance. Using the solvents named above is preferred to increase the polymer usage rate.

Examples of the oxidizing agent used in oxidation polymerization include halogens such as chlorine, bromine, or iodine; metallic halides such as iron(II) chloride, boron trifluoride, arsenic pentafluoride, or antimony pentafluoride; peroxides such as hydrogen peroxide; persulfuric acid and its salts, such as persulfuric acid, potassium persulfate, or ammonium persulfate; halogen acids and its salts, such as iodic acid or potassium perchlorate; transition metallic compounds such as potassium permanganate or chromic acid; protonic acids such as nitric acid or sulfuric acid; ozone; and oxygen. These may be used singly or in combination.

The dopant used in this invention is a generally used acceptor-type dopant. Concrete examples include halogen anions such as chlorine,

bromine, iodine, or hydrogen chloride; halogenated anions such as hexifluorophosphorus, hexafluoroarsenic, or tetrafluoroboron; alkylbenzenesulfonic acid and benzene sulfonic acid anions; perchloric acid anions such as perchloric acid or potassium perchlorate; and sulfuric acid anions such as sulfuric acid. These may be used singly or in combination.

The amount of monomers, oxidizing agents, and dopants during polymerization differs depending on the amount, shape, size, and desired resistance of the toner to be treated, but a conductive polymer can be adhered effectively to core substance grains when the amount of monomers is 0.05 to 30 parts by weight per 100 parts by weight solvent, the amount of oxidizing agents is 0.05 to 30 parts by weight per 100 parts by weight solvent, the amount of dopants is 0.01 to 20 parts by weight per 100 parts by weight solvent, and the amount of core substance is 0.1 to 50 parts by weight per 100 parts by weight solvent. The temperature when polymerizing monomers is preferably -40 to 50°C, and more preferably about -10 to 10°C.

When an iron(II) salt such as iron(II) chloride is used as the oxidizing agent in the method described above, the iron salt contained in the conductive polymer can be converted to a magnetic iron compound by methods known in prior art. An example of such a method is immersing the core substance with the conductive polymer adhered in a solvent containing a pH regulator, applying heat treatment as required, and introducing oxygen gas.

The material comprising the core substance in this invention is formed by mixing components such as a magnetic substance, coloring agent, fluidity improving agent, and charge regulator as required in a

resin component. Examples of resin components include styrene resin, styrene copolymer resins such as styrene-acrylic resin, styrene-butadiene resin, or styrene-maleic acid copolymer resin, and polyethylene, polypropylene, polyester, polyurethane, polyvinyl chloride, epoxy resin, polyvinyl butyral, rosin, modified rosin, paraffin wax, and ketone resin. These can be used singly or in combination. Conductive polymers are generally black and function as a coloring agent by themselves, but there is no objection to also mixing carbon black or another dye or pigment into the core substance as a coloring agent.

When manufacturing the toner of this invention, methods include mixing the material comprising the core substance well by a hot kneading machine such as a hot roller or kneader, then obtaining the core substance by pulverizing or classifying mechanically, and adhering the conductive polymer to this core substance; and mixing the required materials with the monomer that is to comprise the binder resin, then obtaining the toner core substance by polymerizing this emulsified suspension, and adhering the conductive polymer. The grain diameter of the toner should 1 to 50 μm, and preferably about 5 to 15 μm.

The toner of this invention can be used as a two-component developing agent by mixing with a carrier, but to use as a standard one-component developing agent, the core substance should be adjusted by adding a magnetic material. For the magnetic substance, ferromagnetic elements such as iron, cobalt, or nickel, and alloys or compounds containing these such as magnetite, hematite, or ferrite can be used as appropriate. The granularity of these substances is 0.1 to 0.8 μm, and more preferably 0.3 to 0.5 μm. Ideally, the content is 10 to 120 parts

by weight, and more preferably 30 to 100 parts by weight, per 100 parts by weight binder resin.

(Working Examples)

Below, this invention will be explained in detail by working examples, but this invention is not in any way limited to these examples. Moreover, in the working examples, "parts" represents "parts by weight."

Working Example 1

61 parts styrene-butyl acrylate copolymer, 36 parts magnetite, and 3 parts low molecular weight polyethylene wax were mixed. This mixture was heated, fused, and kneaded by a roller mill, and after cooling, was coarsely pulverized by a hammer mill, then finely pulverized using a jet mill. Next, this was classified using a pneumatic classifier, and a core substance with a grain diameter of 8 to 15 μm was obtained.

4.88 parts of this core substance were moistened with 4.88 parts methanol and added to a solution comprised of 61.3 parts water and 8.13 parts iron(III) chloride hexahydrate. This mixture was added to a solution of 0.81 part pyrrole dissolved in 20 parts water while agitating at 0°C, agitated for 3 minutes, and filtered. After washing with water, then methanol, this was dried, and a black conductive magnetic toner was obtained. This toner showed resistance of 3×10^2 Ω-cm. When electrostatic latent images formed on a zinc oxide photosensitive unit were developed using this magnetic toner and images were transferred onto paper, sharp images with no fogging were obtained.

Working Example 2

58 parts styrene-methyl methacrylate copolymer, 36 parts magnetite, 2.5 parts low molecular weight polyethylene wax, and 3 parts carbon

black were mixed. This mixture was treated by the same steps as Working Example 1, and a core substance with an average grain diameter of 12 μm was obtained.

4 parts of this core substance were moistened with 4 parts acetonitrile and added to a solution comprised of 69 parts water, 1.3 parts concentrated hydrochloric acid, and 0.6 part aniline. This mixture was added to a solution comprised of 17.9 parts 1 N sulfuric acid and 3.2 parts ammonium persulfate while agitating at 0°C, and agitated for 20 minutes. After filtering, this was washed with water and methanol, then dried, and a black magnetic toner was obtained. This toner showed resistance of 4×10^5 Ω-cm. When electrostatic latent images formed on a zinc oxide photosensitive unit were developed using this magnetic toner and images were transferred onto paper, sharp images with no fogging were obtained.

Working Example 3

4.88 parts of the core substance obtained in Working Example 2 were moistened with 4.88 parts acetonitrile and added to a solution comprised of 30 parts water, 31.3 parts acetonitrile, and 8.13 parts iron(III) chloride hexahydrate. This mixture was added to a solution of 0.81 part 3-methoxythiophen dissolved in 20 parts acetonitrile while agitating at room temperature, agitated for 30 minutes, and filtered. After washing with water, then methanol, this was dried, and a black conductive magnetic toner was obtained. This toner showed resistance of 6×10^9 Ω-cm. When electrostatic latent images formed on a zinc oxide photosensitive unit were developed using this magnetic toner and images were transferred onto paper, sharp images with no fogging were obtained.

Working Example 4

70 parts styrene-butyl acrylate copolymer, 24 parts magnetite, 2.5 parts low molecular weight polyethylene wax, and 3 parts carbon black were mixed. This mixture was treated by the same method as Working Example 1, and a core substance with a grain diameter of 8 to 15 μm was obtained. Polypyrrole was adhered to the surface of the core substance by treating this core substance in the same way as Working Example 1, and a black magnetic toner was obtained. This toner showed resistance of 6×10^2 Ω-cm. When this toner was placed in a sodium hydroxide aqueous solution, regulated to approximately pH 11, and treated by heating to 90°C for 60 minutes, the iron salt contained in the polypyrrole became a magnetic oxide. This core substance with polypyrrole containing this magnetic oxide adhered was filtered and washed with water, then dried, and a magnetic toner was obtained. This toner showed resistance of 8×10^3 Ω-cm. When electrostatic latent images formed on a zinc oxide photosensitive unit were developed using this magnetic toner and images were transferred onto paper, sharp images with no fogging were obtained.

(Effects of the Invention)

In this invention, a conductive polymer can be adhered to the surface of a core substance comprised of a polymer resin or rubber grains mixed with components such as a coloring agent, magnetic powder, and charge regulator as required using a simple apparatus and by the simple method of agitating in a solution. Part of the conductive polymer complexes with the core substance, and furthermore, generally becomes an extremely thin layer and covers the core substance. As a result, this adheres firmly.

The electrophotographic toner of this invention can be controlled

freely to a resistance of about 1 Ω-cm to 10^{15} Ω-cm. In addition, because the conductive mechanism of the conductive polymer is electron conduction, the toner is stable and completely unaffected by the ambient environment, especially humidity.

Furthermore, because the conductive polymer is generally black and functions as a coloring agent, when an iron(III) salt is used as the oxidizing agent during oxidation polymerization of monomers, magnetism can be imparted to the conductive polymer.

Therefore, this invention can offer an electrophotographic toner at a low price that satisfies toner characteristics when higher function and stability are demanded.